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CHEMICAL STRUCTURES AND COMPOSITIONS OF ECP  
ADDITIVES TO REDUCE PIT DEFECTS

Field of the Invention

[001] The present invention relates to electrochemical plating (ECP) processes used to deposit metal layers on semiconductor wafer substrates in the fabrication of semiconductor integrated circuits. More particularly, the present invention relates to a composition and method for enhancing wetting of electrochemical plating electrolyte to a metal seed layer in electrochemical plating of metals, particularly copper, on a substrate.

Background of the Invention

[002] In the fabrication of semiconductor integrated circuits, metal conductor lines are used to interconnect the multiple components in device circuits on a semiconductor wafer. A general process used in the deposition of metal conductor line patterns on semiconductor wafers includes deposition of a conducting layer on the silicon wafer substrate; formation of a photoresist or other mask such as titanium oxide or silicon oxide, in the form of the desired metal conductor line pattern, using standard lithographic techniques; subjecting the wafer substrate to a dry etching process to remove the conducting layer from the areas not covered by the mask, thereby leaving the metal

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layer in the form of the masked conductor line pattern; and removing the mask layer typically using reactive plasma and chlorine gas, thereby exposing the top surface of the metal conductor lines. Typically, multiple alternating layers of electrically conductive and insulative materials are sequentially deposited on the wafer substrate, and conductive layers at different levels on the wafer may be electrically connected to each other by etching vias, or openings, in the insulative layers and filling the vias using aluminum, tungsten or other metal to establish electrical connection between the conductive layers.

[003] Deposition of conductive layers on the wafer substrate can be carried out using any of a variety of techniques. These include oxidation, LPCVD (low-pressure chemical vapor deposition), APCVD (atmospheric-pressure chemical vapor deposition), and PECVD (plasma-enhanced chemical vapor deposition). In general, chemical vapor deposition involves reacting vapor-phase chemicals that contain the required deposition constituents with each other to form a nonvolatile film on the wafer substrate. Chemical vapor deposition is the most widely-used method of depositing films on wafer substrates in the fabrication of integrated circuits on the substrates.

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[004] Due to the ever-decreasing size of semiconductor components and the ever-increasing density of integrated circuits on a wafer, the complexity of interconnecting the components in the circuits requires that the fabrication processes used to define the metal conductor line interconnect patterns be subjected to precise dimensional control. Advances in lithography and masking techniques and dry etching processes, such as RIE (Reactive Ion Etching) and other plasma etching processes, allow production of conducting patterns with widths and spacings in the submicron range. Electrodeposition or electroplating of metals on wafer substrates has recently been identified as a promising technique for depositing conductive layers on the substrates in the manufacture of integrated circuits and flat panel displays. Such electrodeposition processes have been used to achieve deposition of the copper or other metal layer with a smooth, level or uniform top surface. Consequently, much effort is currently focused on the design of electroplating hardware and chemistry to achieve high-quality films or layers which are uniform across the entire surface of the substrates and which are capable of filling or conforming to very small device features. Copper has been found to be particularly advantageous as an electroplating metal.

[005] Electroplated copper provides several advantages over electroplated aluminum when used in integrated circuit (IC)

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applications. Copper is less electrically resistive than aluminum and is thus capable of higher frequencies of operation. Furthermore, copper is more resistant to electromigration (EM) than is aluminum. This provides an overall enhancement in the reliability of semiconductor devices because circuits which have higher current densities and/or lower resistance to EM have a tendency to develop voids or open circuits in their metallic interconnects. These voids or open circuits may cause device failure or burn-in.

[006] A typical standard or conventional electroplating system for depositing a metal such as copper onto a semiconductor wafer includes a standard electroplating cell having an adjustable current source, a bath container which holds an electrolyte electroplating bath solution (typically acid copper sulfate solution), and a copper anode and a cathode immersed in the electrolyte solution. The cathode is the semiconductor wafer that is to be electroplated with metal. Both the anode and the semiconductor wafer/cathode are connected to the current source by means of suitable wiring. The electroplating bath solution may include an additive for filling of submicron features and leveling the surface of the copper electroplated on the wafer. An electrolyte holding tank may further be connected to the bath

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container for the addition of extra electrolyte solution to the bath container, as needed.

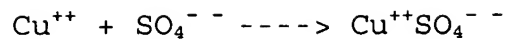
[007] In operation of the electroplating system, the current source applies a selected voltage potential typically at room temperature between the anode and the cathode/wafer. This potential creates a magnetic field around the anode and the cathode/wafer, which magnetic field affects the distribution of the copper ions in the bath. In a typical copper electroplating application, a voltage potential of about 2 volts may be applied for about 2 minutes, and a current of about 4.5 amps flows between the anode and the cathode/wafer. Consequently, copper is oxidized at the anode as electrons from the copper anode and reduce the ionic copper in the copper sulfate solution bath to form a copper electroplate at the interface between the cathode/wafer and the copper sulfate bath.

[008] The copper oxidation reaction which takes place at the anode is illustrated by the following reaction equation:

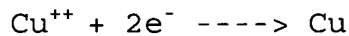


[009] The oxidized copper cation reaction product forms ionic copper sulfate in solution with the sulfate anion in the bath 20:

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[0010] At the cathode/wafer, the electrons harvested from the anode flowed through the wiring reduce copper cations in solution in the copper sulfate bath to electroplate the reduced copper onto the cathode/wafer:



[0011] When a copper layer is deposited on a substrate, such as by electrochemical plating, the copper layer must be deposited on a metal seed layer such as copper which is deposited on the substrate prior to the copper ECP process. Seed layers may be applied to the substrate using any of a variety of methods, such as by physical vapor deposition (PVD) and chemical vapor deposition (PVD). Typically, metal seed layers are thin (about 50-1500 angstroms thick) in comparison to conductive metal layers deposited on a semiconductor wafer substrate.

[0012] Conventional electrochemical plating techniques use copper sulfate ( $\text{CuSO}_4$ ) for the main electrolyte in the electroplating bath solution. The solution may further include additives such as chloride ion and levelers, as well as accelerators and suppressors which increase and decrease, respectively, the rate of the electroplating process. The rate of deposition of copper

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on the substrate, and the quality and resulting electrical and mechanical properties of the metallization, are critically dependent on the concentration of these organic additives in the electroplating bath solution. However, one of the drawbacks of the conventional suppressor used in electroplating bath solutions is that the suppressor causes poor wettability of the solution to the copper seed layer on a substrate. Non-uniform wetting of the solution to the seed layer causes structural defects such as pits in the metal electroplated onto the seed layer, compromising the structural and functional integrity of the finished IC devices fabricated on the substrate. Further, inadequate wetting of the electrolyte solution to gap features results in inadequate filling of the features, particularly with regard to 65 nm copper technology.

[0013] Traditional approaches to improving the wetting of an electrolyte electroplating bath solution to a metal seed layer include pre-rinsing or pre-annealing of the seed layer surface. However, both of these methods achieve unsatisfactory results. Accordingly, a new and improved composition and method is needed for enhancing the wetting of an electroplating bath solution to a metal seed layer in the electrochemical plating of copper or other metal on a substrate.

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[0014] An object of the present invention is to provide a novel composition and method for improving the gap fill characteristics and reducing surface defects of metal electroplated on a substrate.

[0015] Another object of the present invention is to provide a novel composition and method for enhancing the wetting of an electroplating bath solution to a metal seed layer in the electrochemical plating of copper or other metal on a substrate.

[0016] Still another object of the present invention is to provide a novel composition and method which results in electroplating of a metal layer substantially devoid of structural defects on a seed layer provided on a substrate and improves gap fill capability through wetting improvement.

[0017] Yet another object of the present invention is to provide a novel composition which is added to an electroplating bath solution to substantially reduce or eliminate the formation of pits or other surface defects in an electroplated metal and enhance gap fill capability.



### Summary of the Invention

[0018] In accordance with these and other objects and advantages, the present invention is generally directed to a novel composition and method which is suitable to enhance the wetting of an electroplating bath solution on an electroplating surface. Optimum wetting of the electroplating bath solution to the electroplating surface results in an electroplated metal which is substantially devoid of surface pits and other structural defects and is characterized by enhanced gap fill capability. The composition includes a suppressor additive for the electroplating bath solution. The suppressor additive is a copolymer which includes various proportions of ethylene oxide monomer and propylene oxide monomer.

[0019] According to the method of the invention, an electrolyte electroplating bath solution is prepared, and the suppressor additive copolymer is mixed with the bath solution. The substrate having the electroplating surface is immersed in the solution and subjected to electrochemical plating. During immersion of the substrate, the solution, which is characterized by a high capillary rise and low interfacial energy as compared to electroplating bath solutions having a conventional, commercially-available suppressor additive, rapidly wets the electroplating surface. This ensures optimal wetting of all

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regions on the electroplating surface, including high aspect ratio gap features, and results in uniform electroplating deposition and gap-filling with minimal tendency for immersion-related electroplating defects.

#### Brief Description of the Drawings

[0020] The invention will be better understood, by way of example, with reference to the accompanying drawings, in which:

[0021] FIG. 1 is a schematic of an electrochemical plating system in implementation of the present invention;

[0022] FIG. 1A is a cross-sectional view of a substrate with a metal layer electroplated thereon according to the composition and method of the present invention; and

[0023] FIG. 2 is a flow diagram illustrating a typical flow of process steps according to the method of the present invention.

#### Detailed Description of the Invention

[0024] The present invention has particularly beneficial utility in the electrochemical plating of copper on a copper seed layer deposited on a semiconductor wafer substrate in the fabrication of semiconductor integrated circuits. However, the invention is more generally applicable to the electrochemical plating of

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metals including but not limited to copper on substrates in a variety of industrial applications including but not limited to semiconductor fabrication.

[0025] The present invention is generally directed to a novel composition and method for enhancing the wetting of an electroplating bath solution on a seed layer provided on a substrate. The composition and method facilitates the electroplating of a metal which is substantially devoid of surface pits and is characterized by enhanced gap fill capability, on the seed layer. The composition includes a suppressor additive for the electroplating bath solution. The suppressor additive is a copolymer which includes various proportions of ethylene oxide monomer and propylene oxide monomer.

[0026] In one embodiment, the suppressor additive is a block copolymer of ethylene oxide and propylene oxide. In another embodiment, the suppressor additive is a random copolymer of ethylene oxide and propylene oxide. In still another embodiment, the suppressor additive is an alternating copolymer of ethylene oxide and propylene oxide. Preferably, the suppressor additive copolymer comprises at least about 60% by weight ethylene oxide. Most preferably, the suppressor additive copolymer comprises

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about 80% by weight ethylene oxide and about 20% by weight propylene oxide. The suppressor additive copolymer preferably has a molecular weight in the range of from typically about 500 to about 20,000.

[0027] The composition and method of the present invention may be used with any formulation for the electroplating bath solution, such as copper, aluminum, nickel, chromium, zinc, tin, gold, silver, lead and cadmium electroplating baths. The present invention is also suitable for use with electroplating baths containing mixtures of metals to be plated onto a substrate. It is preferred that the electroplating bath be a copper alloy electroplating bath, and more preferably, a copper electroplating bath. Typical copper electroplating bath formulations are well known to those skilled in the art and include, but are not limited to, an electrolyte and one or more sources of copper ions. Suitable electrolytes include, but are not limited to, sulfuric acid, acetic acid, fluoroboric acid, methane sulfonic acid, ethane sulfonic acid, trifluormethane sulfonic acid, phenyl sulfonic acid, methyl sulfonic acid, p-toluenesulfonic acid, hydrochloric acid, phosphoric acid and the like. The acids are typically present in the bath in a concentration in the range of from about 1 to about 300 g/L. The acids may further include a source of halide ions such as chloride ions. Suitable sources of

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copper ions include, but are not limited to, copper sulfate, copper chloride, copper acetate, copper nitrate, copper fluoroborate, copper methane sulfonate, copper phenyl sulfonate and copper p-toluene sulfonate. Such copper ion sources are typically present in a concentration in the range of from about 10 to about 300 g/L of electroplating solution.

[0028] In a preferred embodiment, the suppressor additive composition of the present invention is present in the electroplating bath solution in a concentration of from typically about 50 ppm to about 500 ppm. An accelerator is typically present in the electrolyte bath solution in a concentration of from typically about 2 ppm to about 50 ppm. The accelerator may be any type of commercially-available accelerator known by those skilled in the art for accelerating a metal electroplating deposition process.

[0029] Other electrochemical plating process conditions suitable for implementation of the present invention include a plating rpm of from typically about 0 rpm to about 500 rpm; a plating current of from typically about 0.2 mA/cm<sup>2</sup> to about 20 mA/cm<sup>2</sup>; and a bath temperature of from typically about 10 degrees C to about 35 degrees C. In cases in which planarity of the electroplated metal through chemical mechanical planarization (CMP) is

necessary, a leveling agent may be added to the electroplating bath solution at a concentration of from typically about 5 mmol/L to about 5 mol/L.

[0030] Referring to FIG. 1, an electrochemical plating (ECP) system 10 suitable for implementation of the present invention is shown. The system 10 may be conventional and includes a standard electroplating cell having an adjustable current source 12, a bath container 14, a typically copper anode 16 and a cathode 18, which cathode 18 is the semiconductor wafer substrate that is to be electroplated with copper. The anode 16 and cathode/substrate 18 are connected to the current source 12 by means of suitable wiring 38. The bath container 14 holds an electrolyte electroplating bath solution 20. The system 10 may further include a mechanism for rotating the substrate 18 in the bath 20 during the electroplating process, as is known by those skilled in the art.

[0031] The ECP system 10 may further include a pair of bypass filter conduits 24, a bypass pump/filter 30, and an electrolyte holding tank 34 for the introduction of additional electrolytes into the bath container 14, as necessary. The bypass filter conduits 24 typically extend through the anode 16 and open to the upper, oxidizing surface 22 of the anode 16 at opposite ends of

the anode 16. The bypass filter conduits 24 connect to the bypass pump/filter 30 located outside the bath container 14, and the bypass pump/filter 30 is further connected to the electrolyte holding tank 34 through a tank inlet line 32. The electrolyte holding tank 34 is, in turn, connected to the bath container 14 through a tank outlet line 36. It is understood that the ECP system 10 heretofore described represents just one example of a possible system which is suitable for implementation of the present invention, and other systems of alternative design may be used instead.

[0032] Referring to FIGS. 1, 1A and 2, according to the method of the present invention, a metal seed layer 19, such as copper, is deposited on a wafer substrate 18, as indicated in step S1 of FIG. 2. The metal seed layer 19 may be deposited on the substrate 18 using conventional chemical vapor deposition (CVD) or physical vapor deposition (PVD) techniques, according to the knowledge of those skilled in the art. The seed layer 19 has a thickness of typically about 50-1500 angstroms.

[0033] As indicated in step S2 of FIG. 2, the electrochemical plating (ECP) electrolyte bath solution 20 is prepared in the bath container 14. The electroplating bath solution 20 typically includes an accelerator having a concentration of from typically

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about 5 mmol/L to about 5 mol/L, and may include a leveling agent or additive in a concentration of from typically about 5 mmol/L to about 5 mol/L, as heretofore noted. Next, as indicated in step S3 and shown in FIG. 1, the suppressor additive copolymer 25 of the present invention is added to and thoroughly mixed with the electroplating bath solution 20 to achieve a suppressor additive concentration of from typically about 5 mmol/L to about 5 mol/L. The anode 16 and substrate 18 are then immersed in the bath solution 20 and connected to the adjustable current source 12 typically through wiring 38.

[0034] As indicated in step S4 of FIG. 2, the cathode/substrate 18 is immersed in the bath solution 20. Accordingly, the seed layer 19 on the substrate 18 contacts the bath solution 20. The entire surface of the seed layer 19, as well as gap features on the substrate 18, are thoroughly wetted by the bath solution 20. It will be appreciated by those skilled in the art that the suppressor additive copolymer composition 25 permits optimal wetting of the ECP electrolyte bath solution 20 to the seed layer 19 during immersion of the substrate 18 and throughout the electroplating process, as the bath solution 20 lacks commercially-available suppressor additives which have been shown to hinder the wetting capabilities of an electroplating bath solution.



[0035] As shown in FIG. 1A and indicated in step S5 of FIG. 2, a metal layer (not shown) is electroplated onto the seed layer 19, typically as follows. The electroplating bath solution 20 is heated to a temperature of typically from about 10 degrees C to about 35 degrees C. In operation of the ECP system 10, the current source 12 applies a selected voltage potential, typically at room temperature, between the anode 16 and the cathode/substrate 18. This voltage potential creates a magnetic field around the anode 16 and the cathode/substrate 18, which magnetic field affects the distribution of the copper ions in the bath solution 20. In a typical copper electroplating application, a voltage potential of about 2 volts may be applied for about 2 minutes, and a plating current of from typically about 0.2 mA/cm<sup>2</sup> to about 20 mA/cm<sup>2</sup> flows between the anode 16 and the cathode/substrate 18. The plating rpm for the substrate 18 is typically about 0-500 rpm. Consequently, copper is oxidized typically at the oxidizing surface 22 of the anode 16 as electrons from the copper anode 16 reduce the ionic copper in the copper sulfate solution bath 20 to form a copper electroplate (not illustrated) at the interface between the cathode/substrate 18 and the copper sulfate bath 20. Due to thorough and substantially uniform wetting of the electrolyte bath solution 20 to the entire surface of the seed layer 19, the electroplated metal layer 21 deposited onto the seed layer 19 is substantially

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continuous and devoid of structural deformities such as pits. Furthermore, the electroplated metal is particularly effective in high aspect ratio gap-filling applications. Accordingly, the electroplated metal layer 21 on the substrate 18 contributes to the fabrication of high-quality IC devices that are characterized by high structural and operational integrity.

[0036] While the preferred embodiments of the invention have been described above, it will be recognized and understood that various modifications can be made in the invention and the appended claims are intended to cover all such modifications which may fall within the spirit and scope of the invention.